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**EXPLORATORY INVESTIGATION OF NOBLE
METAL COATINGS FOR CHROMIUM**

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INTRODUCTION

E-4036 Chromium, a body-centered cubic metal which exhibits a sharp temperature transition between ductile and brittle behavior, has a high solubility for nitrogen at high temperatures. At low temperatures, however, the solubility of nitrogen is very small and nitride precipitation occurs. Nitrogen in solution, surface nitrides, and intergranular nitrides embrittle chromium. The mechanisms of embrittlement are not, as yet, fully resolved. It is known, however, that the extent of embrittlement is related to alloy chemistry, grain size, exposure time, exposure temperature, and quench rate after exposure. DMIC Report 234, "Chromium and Chromium Alloys", Oct. 1, 1966 provides a timely summary of this problem.

Alloying of chromium with rare earth additions such as yttrium and/or lanthanum has been shown to inhibit the rate of nitrogen embrittlement at high temperatures. However, such rare earth additions must be limited to very small percentages in order to avoid the formation of low melting eutectics. At allowable levels, such alloy additions do not provide long time protection from nitrogen embrittlement. Thus, in order to provide such protection, coatings capable of stopping nitrogen ingress and minimizing oxidation at elevated temperatures are being sought. Such coatings must not, of course, in themselves embrittle the substrate by interdiffusion with it. NASA-Lewis has funded several contractual efforts to develop suitable coatings for chromium alloys. These included an aluminide, a silicide, and a nickel-chromium cladding approach.

Beside these, an internal program has explored the protection afforded by coatings of platinum, palladium, iridium, and rhenium. This paper describes the available results of this internal program.

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The noble metals were selected, among other reasons, because they reportedly have very low nitrogen solubility (thus decreasing the driving force for inward diffusion of nitrogen) and because they do not form nitrides. Also, they are inherently oxidation resistant. Rhenium, in spite of its poor oxidation resistance, was selected for evaluation because of its very low nitrogen solubility, its reported lack of nitrides, and its ductilizing effect (when present in large atomic percentages) on chromium.

Program

Uncoated chromium alloys, foils of potential barrier metals, and chromium alloys coated with potential barrier metals were exposed for 100 continuous hours at 2000⁰ F to flowing high purity dry nitrogen. Both Cr-5 w/o W and Cr-5 w/o W-0.12/o Y alloys formed nitride scales. The alloy containing yttrium had a scale thickness of only 0.7 mil and no intergranular nitriding as compared to a 4.4 mil scale and extensive intergranular nitriding on the alloy without yttrium.

Foils of Pd, Pt, and Ir, three mils thick, hardened somewhat after 100 hours at 2000⁰ F in nitrogen as compared to foils vacuum annealed for 20 hours at the same temperature. The Re foil softened somewhat. None of the nitrogen exposed foils showed any significant microstructural changes after exposure. Thus, these results generally justified selection of the barrier metals.

Coatings, less than 1 mil thick, of Pd, Pt, and Re were electrolytically brush plated from commercially available proprietary solutions onto approx. 1/2" × 3/4" × 0.050" specimens of Cr-5 w/o W. This alloy was selected to accentuate any potential nitrogen reaction. After plating, specimens were vacuum or argon annealed to improve bonding. In general, the Pt and Pd coatings stopped nitrogen ingress during the 100 hour nitrogen exposure at 2000⁰ F, as judged metallographically. Some intermetallic compounds, namely Cr₃Pt and CrPd, formed as expected, at the coating-substrate interface. In the case of the Pt coated specimens, the Pt diffused down the Cr grain boundaries and made them resistant to etching. The Re plates achieved were very thin - 1 to 2 microns - and were almost completely taken into solution by the substrate during the anneal. These specimens formed a thicker nitride scale and more

extensive grain boundary nitrides after the 100 hour exposure at 2000⁰ F than did the uncoated substrate. Attempts to deposit thicker Re by brush plating or by a commercial electroplating vendor were unsuccessful. Also unsuccessful were attempts by another experienced vendor to deposit iridium from a fused salt bath onto the chromium alloy substrate.

Based on the above results, Pd and Pt electrodeposits of 0.1, 0.5, and 1.0 mil thickness were chosen for further study. These were commercially applied on a limited number of 1/2'' × 1'' × 0.062'' specimens of Cr-5 w/o W-0.1 w/o Y. Metallographic examination of the as-plated specimens indicated that the Pd plated specimens were satisfactory excepting the 1.0 mil specimens which apparently had been plated in two steps and had a discontinuity between layers. Both the 0.5 and 1.0 mil Pt coatings exhibited cracks perpendicular to the interface and extending, in many cases, to the substrate. Thus, to heal coating defects and promote bonding, most specimens were subsequently annealed in argon at a pressure of 380 torr for 20 hours at 2000⁰ F.

After annealing, all thicknesses of Pd looked dense and well bonded. The Pt coated specimens showed a rather large reaction zone due to the Pt diffusion down the grain boundaries. The 0.5 and 1.0 mil Pt coatings appeared to have separated at the coating-substrate interface - the 1.0 mil specimens showing many areas of complete discontinuity. The cracks, originally present in these coatings, however, had healed.

Coated specimens were exposed to very slowly flowing air (1 SCFH) for 100 continuous hours at temperatures of 2000⁰, 2200⁰, and 2400⁰ F. Bare specimens were simultaneously tested. Weight changes were measured but the results were inconsistent due to the complex interaction on weight change of: CrO₃ volatility(-); oxidation of Cr that diffused to the coating surface(+); surface oxide spallation(-); and possible localized substrate oxidation at minor, unhealed flaws(+). For this reason, metallographic observations, supplemented by a limited number of bend angle tests, were used to evaluate the protective ability of the metal coatings. The results of these tests are reported here and summarized metallographically in figures 1(a), (b), and (c).

2000⁰ F

After 100 hours, all of the annealed Pd and the annealed 0.1 mil Pt coatings on the Cr-5 w/o W-0.1 w/o Y substrate showed no metallographically visible surface or internal nitriding. The thicker Pt coatings which had buckled during annealing were only partially protective. On all specimen surfaces, Cr₂O₃ was observed. This indicates that the Cr from the substrate readily diffused through the noble metals in 100 hours and oxidized on the surface. The uncoated substrate, similarly exposed, developed a thin, tenacious surface oxide film but showed no nitriding. Apparently this naturally occurring oxide on the Cr-5 W-0.1 Y alloy is itself relatively impervious to nitrogen under these test conditions.

After such exposure, one specimen of each coatings thickness was bend angle tested at 950⁰ F. All failed in a brittle manner. The DBTT of the uncoated substrate exposed under similar conditions is approximately 900⁰ F. However, argon annealing alone for 100 hours at 2100⁰ F can increase the DBTT of Cr-5 W-0.1 Y to above 1000⁰ F, probably as a result of grain growth during annealing. Thus, thermal exposure both during post-coating anneal and air testing, contributed to the observed loss of ductility and it is not possible at this time to unambiguously assess the effect of the coating, per se, on embrittlement.

2200⁰ F

At 2200⁰ F, the heavy oxide scale which formed on the uncoated specimens separated during cool down. The unconsumed core had decreased 10 mils in thickness to 52 mils but showed no significant nitriding, probably due to the slow diffusion of nitrogen through the heavy oxide layer. Of the metal coated specimens, only the 0.1 mil Pt and the 1.0 mil Pd appeared to have prevented gross nitriding. The latter showed scattered intragranular nitride precipitates but no external scale or intergranular nitrides. Some pull out of CrPd particles was also observed during polishing. Thus, the heavy oxide scale appears to be a better nitrogen barrier at this temperature than the metal coatings but substrate consumption by oxidation is unacceptably high.

2400° F

After 2400° F air exposure, all coated specimens exhibited gross nitriding. In only 24 hours, at this temperature, the uncoated specimen was 2/3 converted to nitride and the residual metal showed complete intergranular nitriding.

CONCLUDING REMARKS

On the basis of this exploratory study, the noble metals Pt and Pd do not appear promising as coatings for long time protection of chromium alloys from nitrogen embrittlement in air at 2200° F or higher. Chromium diffused rapidly through the noble metals at such temperatures. At lower temperatures, such ductile coatings may hold more potential. However, the effectiveness of the Pd and Pt coatings in avoiding embrittlement as a result of air exposure at 2000° F could not be clearly assessed under the conditions of this study.

METALLOGRAPHIC RESULTS AFTER AIR EXPOSURE

2000° F - 100 HR
AIR

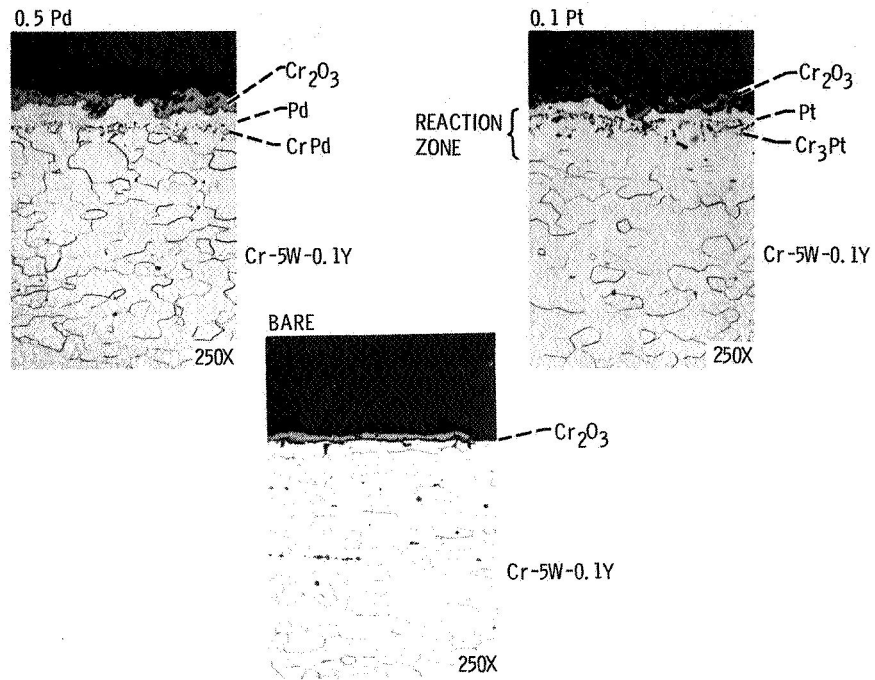


Fig. 1(a).

METALLOGRAPHIC RESULTS AFTER AIR EXPOSURE

2200° F - 100 HR
AIR

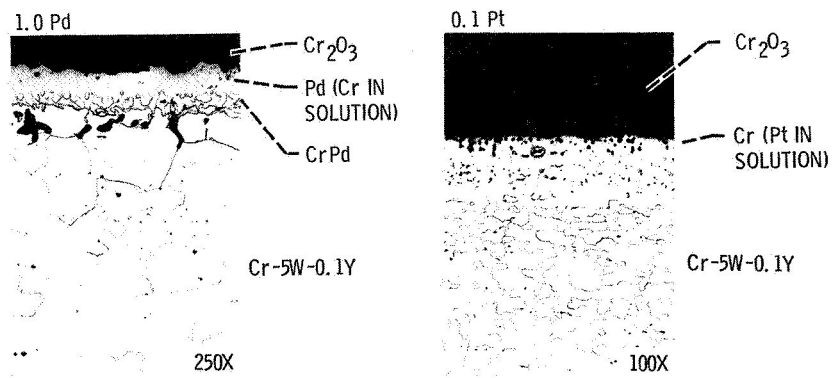


Fig. 1(b).

METALLOGRAPHIC RESULTS AFTER AIR EXPOSURE

2400° F - 100 HR
AIR

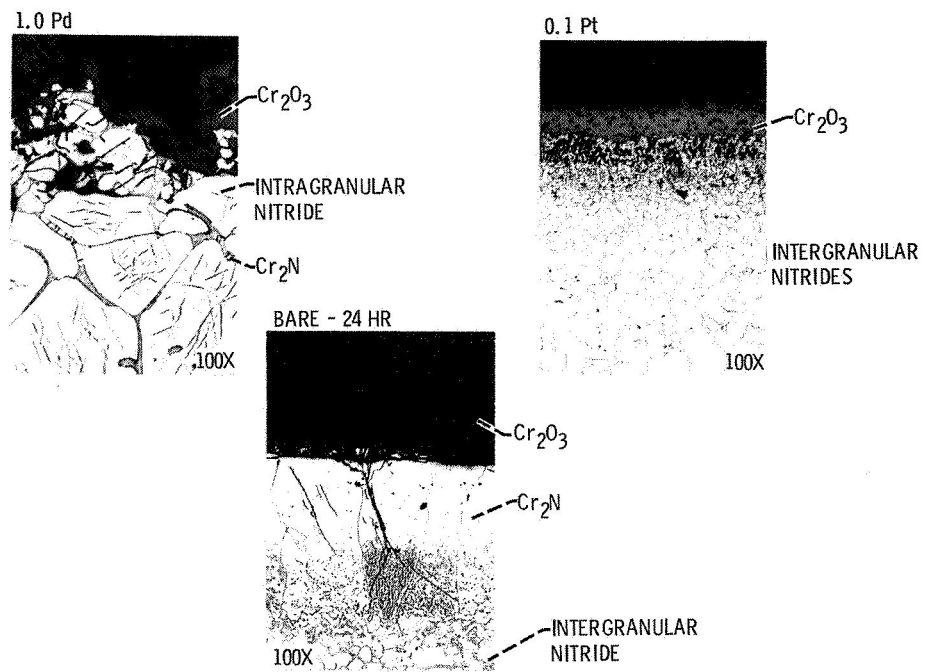


Fig. 1(c).